NIOBIUM

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TRANSLATION

STUDYING THE OXIDATION OF NIOBIUM BASE ALLOYS
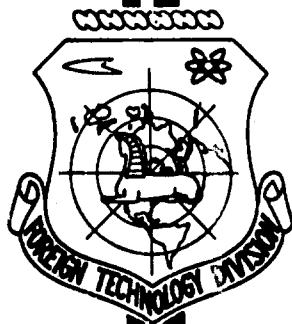
By

V. I. Grigorovich and A. I. Dedyurin

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STUDYING THE OXIDATION OF NIOBIUM BASE ALLOYS

By

V. I. Grigorovich and A. I. Dedyurin

Published investigations of the heat resistance of binary niobium base alloys showed, that during oxidation niobium alloys with 30-35% Zr[1] are oxygen contaminated to a relatively low degree [1]. In this connection it is known, that additions of titanium, vanadium, chromium and molybdenum most effectively raise the scaling resistance of niobium [2]. In this connection it was decided to investigate the combined effect of alloying elements, increasing the resistance to oxygen contamination, and additions, increasing the scaling resistance of niobium.

Investigated was the effect of additions (2-10%) of titanium, vanadium, chromium and molybdenum to an niobium alloy with 30% Zr on the kinetics of oxidation and the diffusion oxygen contamination of the surface layer.

Table 1. Composition of investigated niobium base alloys

No.	Nominal content of alloying elements AT.%	WEIGHT %	Chemical analysis data weight. %
	0 (niobium)	0 (niobium)	
1			
2	30 Zr	29,6 Zr	—
3	30 Zr + 2 Ti	29,9 Zr + 1,045 Ti	31,3 Zr + 1,04 Ti
4	30 Zr + 5 Ti	30,3 Zr + 2,65 Ti	31,1 Zr + 3,0 Ti
5	30 Zr + 10 Ti	31,2 Zr + 5,44 Ti	31,8 Zr + 5,5 Ti
6	30 Zr + 2 V	29,9 Zr + 1,11 V	1,26 V
7	30 Zr + 5 V	30,3 Zr + 2,82 V	3,11 V
8	30 Zr + 10 V	31,1 Zr + 5,77 V	4,8 V
9	30 Zr + 2 Cr	29,9 Zr + 1,13 Cr	30,9 Zr + 1,18 Cr
10	30 Zr + 5 Cr	30,3 Zr + 2,88 Cr	32,1 Zr + 3,1 Cr
11	30 Zr + 10 Cr	31,0 Zr + 5,88 Cr	30,8 Zr + 6,5 Cr
12	30 Zr + 2 Mo	29,6 Zr + 2,075 Mo	1,98 Mo
13	30 Zr + 5 Mo	29,6 Zr + 5,18 Mo	5,05 Mo
14	30 Zr + 7 Mo	29,6 Zr + 7,2 Mo	7,75 Mo
15	30 Zr + 10 Mo	29,6 Zr + 10,32 Mo	9,96 Mo
16	30 Zr - 2 Ce	29,3 Zr + 2,85 Ce	
17	10 Zr + 10 Ti	10,3 Zr + 5,4 Ti	5,76 Ti
18	10 Zr + 10 Mo	9,82 Zr + 10,3 Mo	9,94 Mo
19	10 Zr + 10 Ti + 10 Mo	10,3 Zr + 5,4 Ti + +10,8 Mo	
20	10 Ti + 10 Mo	5,41 Ti + 10,8 Mo	
21	10 Ti + 20 Mo	5,30 Ti + 21,6 Mo	

Here and further on composition of alloys is gien in at. %.

It was kept in mind, that combined alloying with two admixtures may increase the scaling resistance of niobium more effectively, than the alloying with one element in the very same amounts.

The composition of the investigated alloys is shown in table 1.

Experimentation Method

Niobium base alloys were melted out in form of small ingots weighing 35-40 g in an arc furnace with a tungsten electrode, over a copper,water cooled hearth, in a_n argon atmosphere. To eliminate heterogeneities of the ingot the alloys were remelted 6 times.

Chemical analysis of the alloys (see data in table 1) showed a slight discrepancy between the nominal and actual content of alloying admixtures. For the melting was used powdered-metal niobium, which was first remelted to eliminate the spattering of the metal at the time of smelting. In role of alloying materials was used zirconium iodide , electrolytic chromium, carbon thermal vanadium, sheet molybdenum. The purity of the alloying materials and niobium is given in table 2.

Table 2. Chemical Composition of Initial Materials

Material	Content of admixtures, weight %
Niobium in small bars	$(Nb + Ta) - 99,78$; $Ti - 0,06$; $Fe - 0,07$; $S - 0,09$
Zirconium iodide	$Zr - 99,7$; $B < 3 \cdot 10^{-4}$; $L < 2 \cdot 10^{-4}$; $Hf - 0,042$; $N_2 - 0,006$; $Ni < 0,001$; $J < 0,005$; $Mo < 0,01$; $C < 0,05$; $Cd < 3 \cdot 10^{-4}$; $Cl_2 < 0,0025$; $Mn < 0,0002$; $Ti - 0,003$; $Cr < 0,003$; $K < 3 \cdot 10^{-3}$; $Ca < 0,03$; $W < 0,004$; $Cu - 0,001$; $Fe - 0,033$; $Si < 0,05$
Titanium iodide	$Ti - 99,7$; $Fe - 0,01$; $Mg - 0,01$; $Al < 0,02$; $Si - 0,01$; $C - 0,02$; $N_2 - 0,03$; $O_2 - 0,04$; $H_2 - 0,002$; $Mn - 0,06$; $Cr - 0,013$; $Ni - 0,15$

Table 2 , continued

4.Carbon thermal vanadium

V — 99,86; Fe — 0,013; O_2 — 0,036; Al —
0,019; C — 0,48; S — 0,04; N_2 — 0,015;
Si < 0,01; Sb, Sn, Bi, Cd, P < $1 \cdot 10^{-4}$

5.Electrolytic chromium

99,7% Cr

Mo — 99,7; Ni — 0,004; ReO_2 — 0,03;
SiO_2 — 0,002; следы CaO + MgO
следы

6.Sheeted molybdenum

The study of the oxidizability of alloys was made on casted samples 15 mm in
diameter, 6 mm heigh, cut out from billets casted in an arc furnace in copper casting
molds and subjected to preliminary annealing in a TVV-2 vacuum furnace at a tempe—
rature of 1500° for a period of 1 hour.

The samples were oxidized in open air at temperatures of 500 and 1000° at expo-
sures of 1,2,3,5,10 and 20 hours. Prior to oxidation/ the samples/ were subjected to
buffing and electro polishing with a reagent,composed of 150 cm^3 HF and 850 cm^3 H_2SO_4.

Oxidation of samples at a temperature of 500° was done in a tubular furnace in
quartz vessels, at 1000° in a silit furnace and corundum crucibles. The vessels and
crucibles were lid covered. The temperature on the samples was controlled with an
accuracy of ± 5° with a platinum-platinum-rhodium thermocouple, situated near the
samples, and with the MP-28 millivoltmeter.

The oxidizability of the samples was determined by the total gain (overweight),
relative to the surface of the sample (in g/m^2) and by the rate of oxidation within
20 hours (in $g/m^2 \cdot hr$).

On species of all alloys at room temperature was measured the hardness on the
TP device with a diamond pyramid under a 20 kg load. Measured was also hot hardness
of the alloys at temperatures of 500 and 1000° on the VIM-1 device with a load of
1/ kg./

—2 Oxygen contamination was investigated on all alloys which underwent examination/
at a temperature of 1000° for a period of 20 hrs. The depth of oxygen contamination

of the alloy was determined by the method of measuring the microhardness on slides, prepared from sample halves, remaining after the oxidation (cleaned of scales). Prior to measuring the microhardness the slides were subjected to electrolytic polishing in a reagent consisting of 150 cm^{3}HF + 850 cm^3 H$_2$SO$_4$.

Microhardness was measured from the tip of the microsection to its center, using the FMT-3 device with a load of 100 g and 10 sec. exposure. As the depth of oxygen penetration into the alloy was accepted the distance from the tip of the microsection to the point, where microhardness coincided with the initial microhardness of the alloy. From samples of alloys, having undergone tests at 1000° for 20 hrs, was removed the scaling and with the aid of a micrometer was measured the height of the remaining sample, so as to determine the /layer/ of the oxidized metal.

Simultaneously was investigated the microstructure of the oxygen contaminated layer, which showed, that the layer of the contaminated metal in all alloys, containing zirconium, is sharply limited as result of greater structural difference of contaminated and uncontaminated metal. The exception here was pure niobium.

The visible depth of oxygen penetration in the alloys coincides with /the depth/, determined by the microhardness method. This offered the possibility to determine on many alloys /the depth/ of oxygen penetration into the alloy by the direct microscopic method after etching with a reagent consisting of 150 cm^{3}HF + 850 cm^3 H$_2$SO$_4$.

Experimental Results

Measurement of hardness of annealed alloys at room temperature showed, that alloying of niobium considerably raises the /strength/. Unalloyed niobium /had/ a hardness of 150 Hv units, the introduction of 30% Zr increased same by almost double.

Complex alloying of niobium with 30% Zr and admixtures of titanium, vanadium, chromium and molybdenum in the amounts of from 2-10% results in an additional reinforcement of the alloy (fig.1), while alloying with titanium only slightly rises

the hardness of the alloy, and the introduction of chromium, vanadium and molybdenum leads to considerable reinforcement. At a 10% admixture content most ~~effective is~~ Cr, followed by V and Mo. Ternary niobium alloys with 10% Zr and 10% Ti or molybdenum had a hardness of 258 and 285 Hv units respectively.

Hardness of niobium alloys with 10% Ti and 10-20% Mo (20-21), as well as the hardness of the alloy with a 10% Zr admixture (No.19) varied between 303-323 Vickers units.

The results of measuring hot hardness at 500 and 1000° of pure niobium and its alloys are given in table 3 for the purpose of estimating their heat resistance.

With a rise in temperature to 500° the hardness of niobium remains practically unchanged. A further rise in temperature to 1000° leads to a reduction in hardness to 83 kg/mm². Addition of 30% Zr to the niobium raises hot hardness considerably.

Additional alloying of the binary alloy with additions (2-10%) of titanium, vanadium, chromium or molybdenum further rises the heat resistance of alloys at 500°. At a temperature of 1000° additions (2-5%) of titanium, vanadium or chromium to the binary niobium alloy with 30% Zr practically do not raise its hardness. The most effective increase in heat resistance of the binary alloy is offered by an addition of molybdenum, an increase of which in
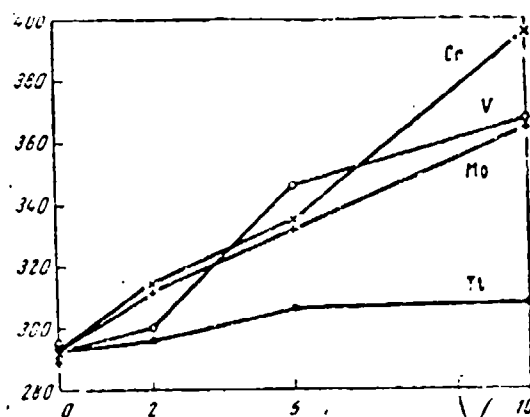

Fig.1. Change in hardness of binary niobium alloy with 30% Zr depending upon the content of alloying admixture titanium, vanadium, chromium and molybdenum. a-Hardness Hv; b-content of admixture, %.

the binary niobium alloy with 30% Zr noticeably raises hot hardness of the alloy at 1000°.

Table 3. Hardness of Niobium Alloys

Composition of alloy at.%	Hardness kg/mm²		Composition of alloy at.%	Hardness kg/mm²	
	at 500°	at 1000°		at 500°	at 1000°
Niobium			30 Zr + 10 V		
30 Zr	153	83	30 Zr + 2 Cr	348	146
30 Zr + 2 Ti	258	184	30 Zr + 5 Cr	309	160
30 Zr + 5 Ti	260	134	30 Zr + 10 Cr	319	134
30 Zr + 10 Ti	265	165	30 Zr + 2 Mo	342	149
30 Zr + 2 V	291	139	30 Zr + 5 Mo	267	168
30 Zr + 5 V	293	149	30 Zr + 10 Mo	292	191
	315	150		342	220

It should be pointed out, that with a rise in temperature to 500° there is only a slight drop in the hardness of the investigated alloys, but a rise in temperature to 1000° results in an essential drop in hardness.

Oxidation of, $\underline{niobium}$/ in air at 500°, as shown by fig.2, occurs by the linear law, which $\underline{indicates}$/ , that the forming weak and porous oxide layer does not protect against $\underline{oxidation}$/ . The formation of such a porous oxide layer on niobium leads to greater rates of oxidation (of the order of 22 g/m².hr) even at 500°, as is evident from data given below. The addition of 30% Zr sharply raises scaling resistance³ as result of formation of a protective oxide layer, and the oxidation $\underline{curves}$/

Fig.2. Change in gains at 500° depending upon exposure time. 1-niobium; 2-Nb+30% Zr; 3-Nb + 30% Zr + 10% Ti. a-gain...b-time hrs.

acquire the form of parabolas. In fig.3
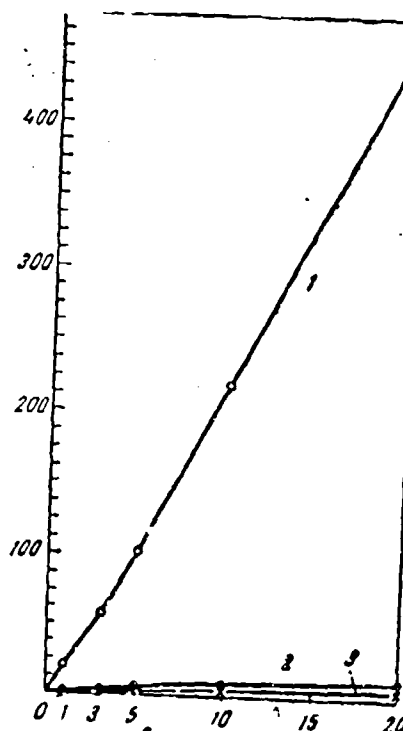
are given the results of testing the oxidation of alloys at 500°. As is evident, sca-
ling resistance of the binary niobium alloy with 30% Zr rises already at additions
of 2% of alloying elements, an increase in the content of these elements to 10%
leads to a further rise in oxidation resistance. A certain deviation from this rule
appeared on alloys with vanadium, where the increase in the vanadium content from
5 to 10% resulted in a small rise in the oxidizability of the alloy. The intersec-
tion of gain curves at small exposures, apparently, is due to the slight difference
in the oxidation of alloys and very small gains, which decreases the accuracy of de-
termination.

The parabolic nature of gain curves at 500° points toward the protectiveness of
the oxide layer, forming on the alloys. On samples of ternary alloys after one hour
of oxidation at a temperature of 500° was formed a dense polished oxide layer, well
preserved even after a 20-hr test. The film on the niobium alloy with 30% Zr after
a 20 hr test acquired a whitish deposit.

Composition of alloys at.%	Rate of oxidation of Ni alloys on air at 500°, g/m²·hr	Composition of alloys at.%	Rate of oxidation of Ni alloys in air at 500°, g/m²·hr
Niobium			
....	22,35	30 Zr + 10 V	0,387
30 Zr	0,528	30 Zr + 2 Cr	0,384
30 Zr + 2 Ti	0,409	30 Zr + 5 Cr	0,337
30 Zr + 5 Ti	0,375	30 Zr + 10 Cr	0,297
30 Zr + 10 Ti	0,339	30 Zr + 2 Mo	0,411
30 Zr + 2 V	0,334	30 Zr + 5 Mo	0,400
30 Zr + 5 V	0,341	30 Zr + 7 Mo	0,347

The outer appearance of certain species after 20-hr oxidation at 500° is shown
in fig.4. On pure niobium already after one hour of testing is formed a white oxide
film, which peels off during the cooling of the sample. Further oxidation leads to
repetition of this process. Alloying of niobium with 30% Zr leads to the formation
of a dense, polished oxide film, which becomes even more stronger upon the introduc-

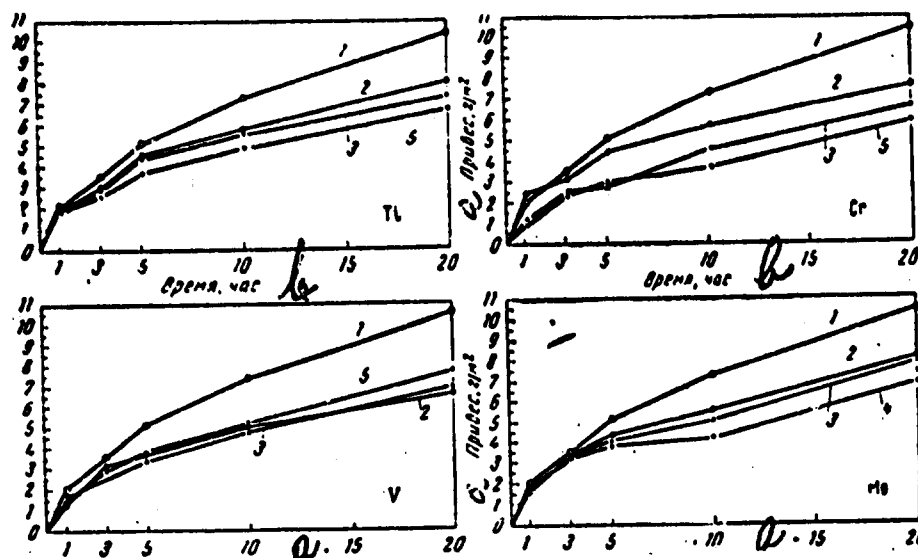tion of titanium, vanadium, chromium and molybdenum admixtures.

Fig.3.Change in gains at 500° of the binary niobium alloy with 30% Zr, additionally alloyed with 2-10% titanium, vanadium, chromium or molybdenum in relation to exposure time. 1-0%; 2-2%; 3-5%; 4-7%; 5-10%; a-gain; b-time/hr.
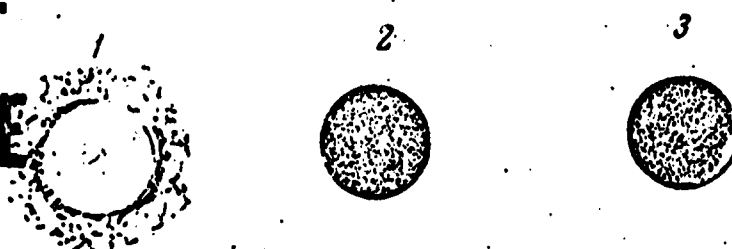

Fig.4.Outer view of samples after oxidation at 500° for 20 hrs.
1-niobium; 2-Nb+30% Zr; 3-Nb+30%Zr + 10% Ti.

In fig.5 are given the rates of oxidation of the investigated alloys in relation to the content of the alloying admixture. Introduction into the binary alloy of 2% titanium, vanadium, chromium or molybdenum results in a sharp reduction in rate of oxidation at 500°. Additions of V and Cr are somewhat more affective than titanium and molybdenum additions. An increase in titatnium, chromium and molybdenum content to 7-10% promotes a further reduction in the rate of oxidation, and a rise in vanadium content to 5-10 at.% results in an increase in the rate of oxidation.
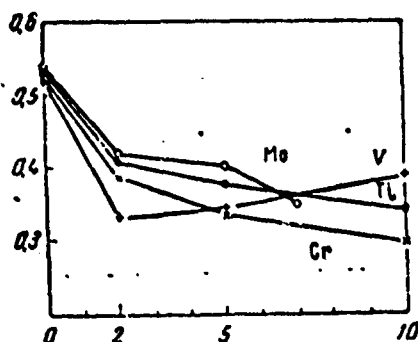
Fig.5.Rates of oxidation at 500° of the binary niobium alloy with 30% Zr depending on the content of titanium,vanadium,chromium or molybdenum admixture.a-rate of oxidation g/m^2.hr; b-content of admixture at.%.

Fig.6.Change in gains at 1000°; 1-niobium 2-Nb+30%Zr; 3-Nb+30%Zr +10%Ti; 4-Nb+30% Zr+7%Mo; Nb+10%Zr+10%Mo+10%Ti; a-gain

Alloying of niobium with 30% Zr raises

its scaling resistance by 45 times,and theb-time.hr.

addition of 10% Ti to this alloy increases its stability in comparison with niobium

by approximately 60 times (see fig.2). Additions of remaining investigated elements

act almost as effectively.

studying/

In fig.6 are given results of/ the oxidation of niobium at 1000°, which

show, that niobium oxidizes extremely intensively, but by the parabolic law. Such

a nature of niobium oxidation is, possibly, due to the calcination of niobium pent-

oxide at 1000°, which promotes the appearance of a certain protectiveness of this

thickened layer.

The addition of 30% Zr somewhat reduces the rate of oxidation, which, however,

still

remains very high, as is evident from the data given below:

In fig.7 are given results of testing the oxidation of alloys at 1000°.Up to 10%

additions of titanium and chromium, up to 5% of vanadium and up to 7% of molybdenum

alloy/

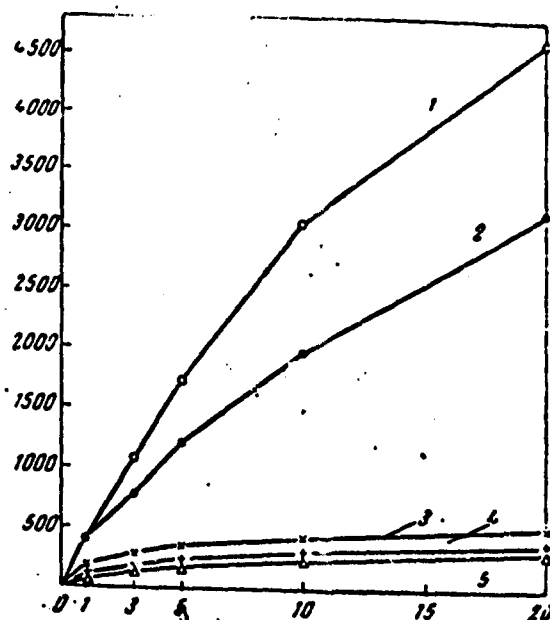considerably improve the scaling resistance of the binary niobium / with 30% Zr.

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Table, page 222

Composition of alloys at.%	Rate of oxidation of Nb alloys in air at 1000°, g/m².hr	Composition of Nb alloys at.%	Rate of oxidation of Nb alloys in air at 1000° g/m².hr
Niobium	229,9	30 Zr + 2 Mo	08,5
30 Zr	157,4	30 Zr + 5 Mo	36,3
30 Zr + 2 Ti	62,9	30 Zr + 10 Mo.	39,5
30 Zr + 5 Ti	46,6	30 Zr + 2 Ce	206,2
30 Zr + 10 Ti	25,8	10 Zr + 10 Ti	40,3
30 Zr + 2 V	63,5	10 Zr + 10 Mo	81,5
30 Zr + 5 V	34,1	10 Zr + 10 Ti + 10 Mo .	16,4
30 Zr + 10 V	236,2	10 Ti + 10 Mo	154,5
30 Zr + 2 Cr	133,9	10 Ti + 20 Mo	143,0
30 Zr + 5 Cr	111,6	30 Zr + 7 Mo	18,9
30 Zr + 10 Cr	-57,8		

It should be pointed out, that already additions of 2% titanium, chromium, vanadium and molybdenum lead to a rise in scaling resistance of the alloy. Less effective in this respect is the effect of chromium. An increase in molybdenum content to more than 7% and vanadium to more than 5% noticeably raises the oxidizability of the alloys.

Results of oxidizing the remaining investigated alloys at 1000° are presented in fig.8. Most intensively oxidized /is the/ Nb alloy with 30 at.% of Zr and 2 at.% Ce. An increase in molybdenum content from 10 to 20% in the Nb alloy with 10% Ti (curves 2 and 3) does not improve scaling resistance. Complex alloying of Nb with 10% Zr, 10% Ti and 10% Mo (curve 6) offers the best result in comparison with other alloys, shown in fig.8.

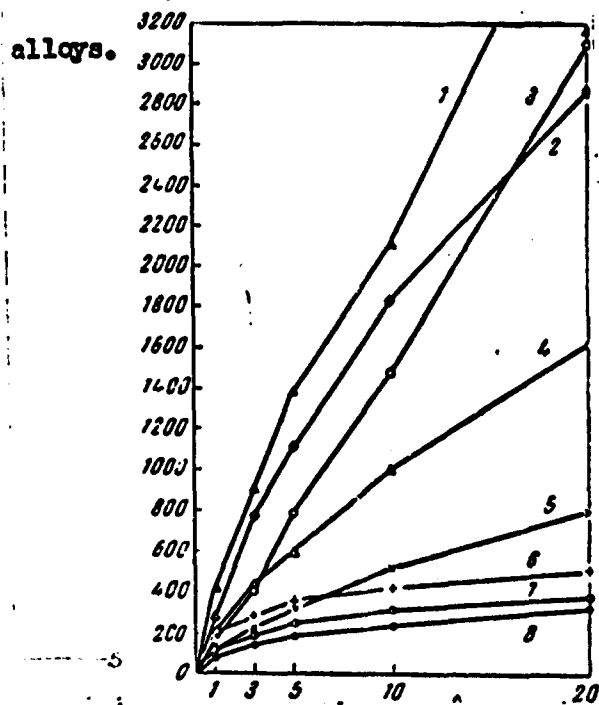Fig.8. Change in gains at 1000° of complex alloyed niobium alloys in relation to exposure time. a-gain; b-time, hr.

add explanations

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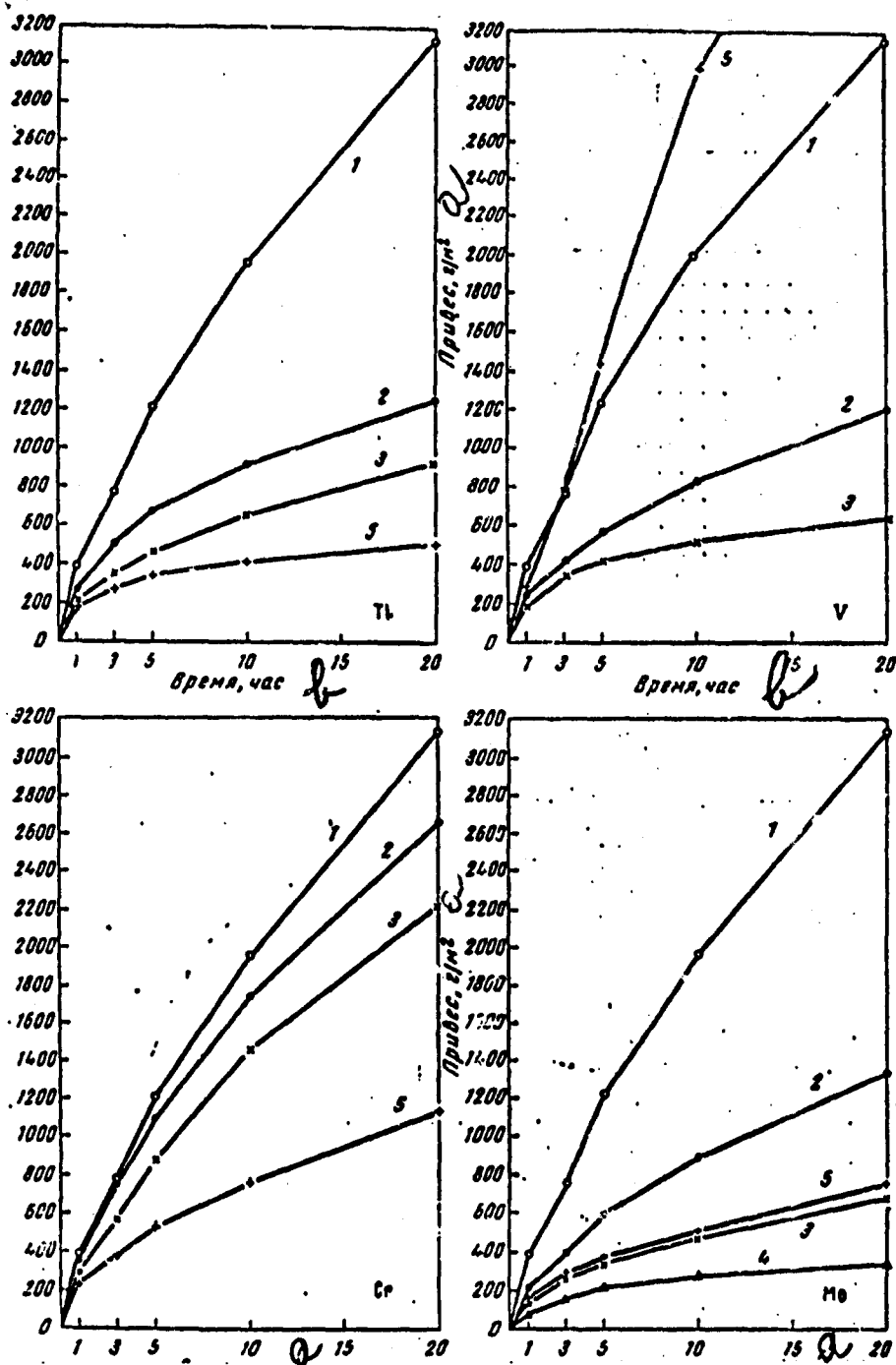
Fig.7. Change in gains at 1000° of the binary Nb alloy with 30% Zr, additionally alloyed with 2-10% titanium, vanadium, chromium, or molybdenum depending upon the exposure time.

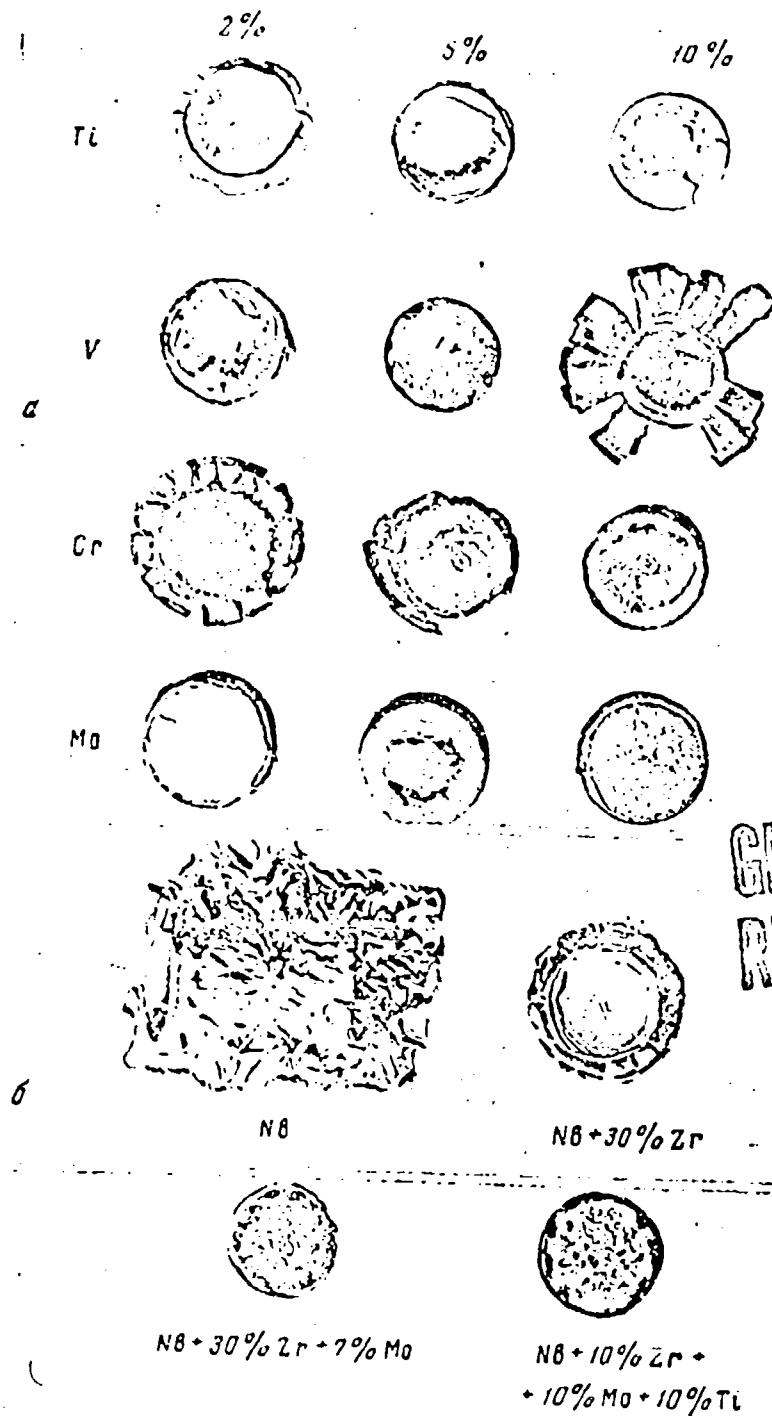1- 0%; 2-2%; 3-5%; 4-7%; 5-10%

a-gain; b-time/hr.

Fig.9. Outer appearance of samples after testing at 1000° for a
period of 20 hours.

The effectiveness of increasing the scaling resistance of niobium upon its alloy ing is well evident from fig.6, where scaling resistance of niobium and the binary niobium alloy with 30 at % Zr is given at 1000° in comparison with the best alloys, having shown minimum gains among all the tested compositions. By alloying is possible to considerably increase the scaling resistance of Nb at 1000°. The best alloy has a scaling resistance 15 times higher than niobium.

The outer appearance of samples of tested alloys after 20 hrs of exposure at 1000° is shown in fig.9. The niobium sam ple with a diameter of 15 mm and 6 mm in height is completely oxidized after / *such* a test. The Nb alloy with 30% Zr is coated with a thick bright-yellow cracking film. A majority of samples of tested alloys has a thick cracking and peeling oxide film. As the content of second alloying element in the binary niobium alloy with 30% Zr increases the thickness of the oxide lay- er decreases. The exception here is the niobium alloy sample with 30 at.% Zr and 10 at.% V, which oxidizes more intensively. During the oxidation on the niobium alloy samples with 30%Zr and 10% Ti,as well as on the niobium alloy with 30% Zr and 5% V is formed a thin peeling off oxide film.

The niobium alloy with 30% Zr and 10% Mo

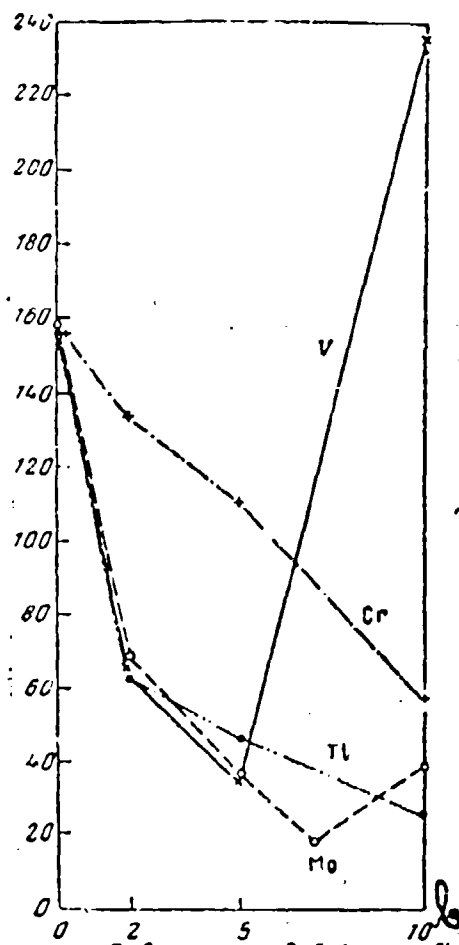Fig.10. Change in rate of oxidation at 1000° of the binary Nb+30%Zr alloy in rela- tion to the content of alloying titanium, vanadium, chromium and molybdenum admixture. a-rate of oxidation, g/m²·hr; b-admixture content at.%.

is covered with a dense non-peeling oxide film,cracking only along the edges of the sample. On the/ <u>niobium/</u> alloy with 30% Zr and 7% Mo, as well as on the niobium alloy with 10% Zr, 10% Mo and 10% Ti, showing minimum gains, is formed a thin dense non-peeling oxide layer of grayish-steel color. The outer appearance of the samples is in good agreement with alloy oxidation curves, having parabolic nature.

Additions of various alloying elements to the binary alloy change the color of the oxide film. Oxides on alloys, alloyed with titanium,have a dirty white color. The brownish color of oxides is characteristic for alloys alloyed with vanadium. Alloys alloyed with chromium, in proportion to its change in content,change the color of oxides from brightly to dirty green . Alloying with molybdenum adds a bright grcish color to the oxides.

In fig.10 are shown the rates of oxidation of the niobium alloy with 30 at.% Zr in relation to the content of titanium, vanadium, chromium and molybdenum admixtures. Additions of 2% titanium, vanadium or molybdenum sharply reduce the rate of alloy oxidation. The effect of Cr is much weaker. Up to a 5% content the effect of titanium, vanadium and molybdenum on the rate of oxidation of the binary alloy is approximately <u>identical./</u>
. Alloys with vanadium admixtures reveal a sharp rise in the rate of oxidation at a vanadium content of over 5%, alloys with molybdenum admixtures - at a content of more than 7%. An increase in the/ <u>titanium/</u> content leads to a continuous reduction in the rate of oxidation, more intensive,than in case of Cr admixtures.

Results of measuring the microhardness of alloys after a 20 hrs exposure at 1000° are given in fig.11. A change in microhardness from the edge toward the center of pure niobium samples (curve 9) and of the binary niobium alloy with 30% Zr (curve 8) shows, that the depth of oxygen penetration into the Nb reaches 4.5 mm, but the alloying of niobium with 30% Zr by admixtures of Ti, Cr or V leaves the depth of oxygen penetration practically unchanged. Depths of oxygen penetration for all alloys are

given in table 4 and constitute about 0.3 - 0.45 mm. A reduction in zirconium content in niobium alloys to 10% leads to an increase in the depth of oxygen penetration.

Table 4. Depth of Oxygen Penetration and Thickness of Metal Layer which converted into scale

Composition of alloy at.%	depth of pene trat. mm	Thickness of metal layer converted in to scale,mm	Composition of alloy at.%	depth of pene trat mm	Tickness of metal layer converted into scale mm
Niobium					
30 Zr	4,5 0,33	−0,64	30 Zr + 10 Cr	0,30	−0,06
30 Zr + 2 Ti	0,39	−0,1	30 Zr + 2 Mo	0,34	−0,25
30 Zr + 5 Ti	0,44	−0,06	30 Zr + 5 Mo	0,35	+0,08
30 Zr + 10 Ti	0,45	+0,03	30 Zr + 7 Mo	0,35	+0,04
30 Zr + 2 V	0,51	−0,07	30 Zr + 10 Mo.	0,42	+0,010
30 Zr + 5 V	0,44	+0,14	10 Zr + 10 Ti	0,51	—
30 Zr + 10 V	0,07	−1,94	10 Zr + 10 Mo.	0,70	—
30 Zr + 2 Cr	0,40	−0,21	10 Zr + 10 Ti + 10 Mo	0,35	—
30 Zr + 5 Cr	0,32	−0,14	10 Ti + 20 Mo.	0,30	—

The oxidation of the alloys is characterized by two processes:penetration of oxygen into the metal and oxidation/ of the/ surface layer of the metal with the formation of scale. In fig.12 are given the combined graphs of oxygen penetration depths into the metal and layer of the metal,which converted into scale within 20 hrs at 1000°, depending upon the content of alloying admixture to the binary Nb alloy with 30% Zr. It is evident from the graphs,that the smallest the / metal/ layer which/ converted into scale, the greater is the depth of penetration of the oxygen: the exception are alloys with chromium,in which the depth of oxygen penetration in dependence upon the chromium admixture to the binary alloy remains almost constant,in spite of the reduction / in/ thickness of the metal layer,which converted into scale. An increase in Ti, Cr and Mo content from 2 to 10% and the content of V to 5% leads to a reduction in the thickness of the metal layer,which transforms into scale.

In fig.13 is shown the initial microstructure of the niobium alloy with 30% Zr, representing a solid, niobium base solution with small separations along the grain

boundaries, which, apparently, are due to contamination of the Nb, *with* oxygen,nitro

gen and other impurities.
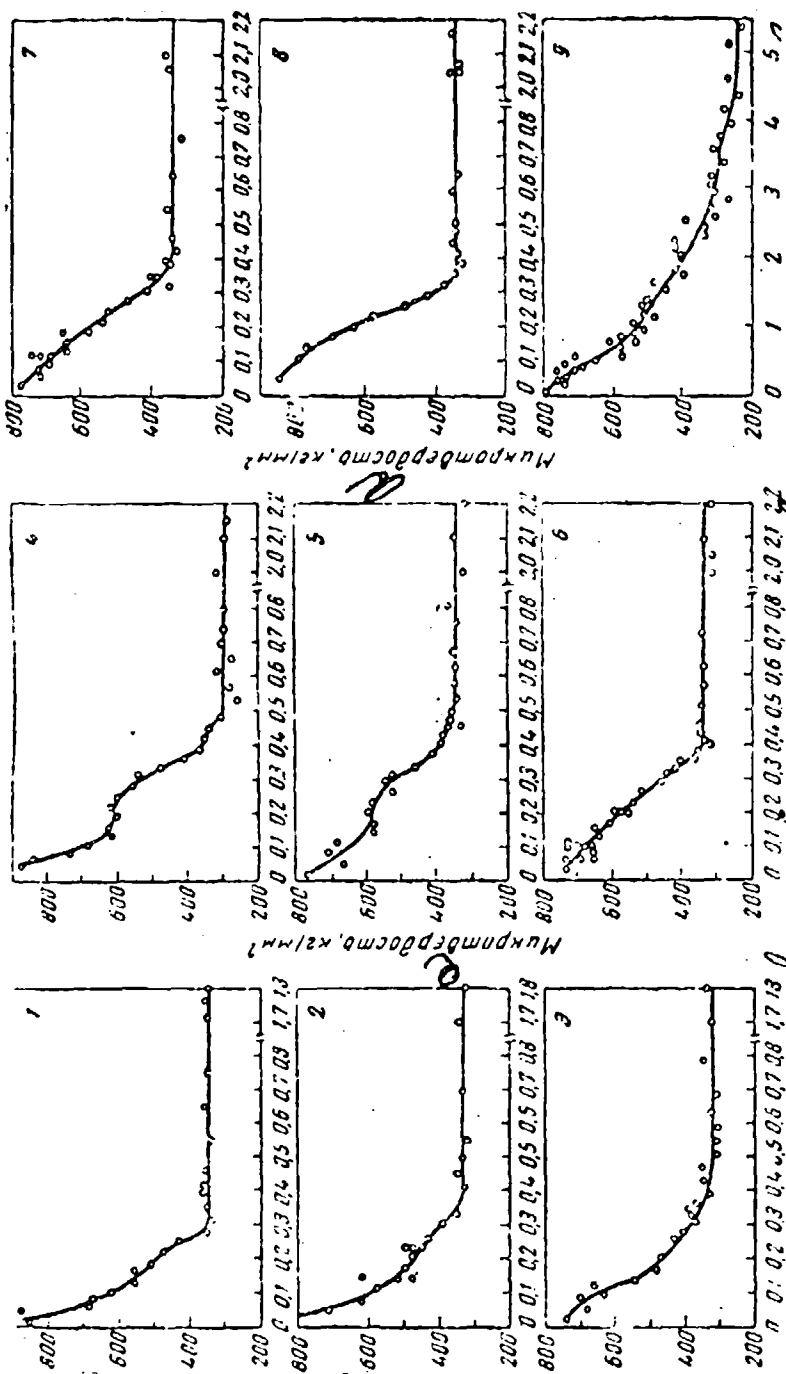
Fig.11.Change in oxygen penetration depth in binary niobium alloy with 30% Zr at 1000°

for 20 hrs, during its alloying:

insert 1 - 7.........

9-pure niobium, a-microhardness; b-distance from edge, mm.

8-without additions (binary alloy with 30% Zr);

Fig.12.Change in oxygen depth penetration (1) and in the layer of the metal which transformed into scale (2) on the binary Nb+30 Zr alloy depending upon the content of alloying titanium, vanadium, chromium and molybdenum admixtures a-depth in mm; b-metal layer, mm; c-admixture....at.%.

Alloying this alloy with titanium and molybdenum admixtures reduces somewhat the number of those separations; but in case of alloying with V and Cr admixtures /their/ number rise considerably. The general nature of the microstructure remains here unchanged.

Fig.13. Initial microstructures of alloys (X 500)
- Nb + 30% Zr; b-Nb + 30% Zr + 10% Ti; c-Nb + 30% Zr + 5% V.

One hours annealing of alloys at 1500° led to the formation of a substructure in the interior of large grains,originating during the solidification of the ingots. A study of the microstructure of a contaminated layer showed, that in the case of unalloyed metal the contamination layer represents a solid oxygen solution in niobium (fig.14a). Alloying of niobium with 30% Zr (fig.14b) sharply changes the microstructure of the layer,contaminated with oxygen; the layer acquires a lamellar structure and is divided into two sub layers - gray (with a more dispersion structure) and a bright one (with less dispersed ; lamellar/ structure). Introduction into the niobium + 30% Zr alloy of admixtures of 2-10% Ti, V, Cr, or Mo does not noticeably change the structure of the layer,contaminated with oxygen. The lamellar structure of the oxidized layer, reminding of an eutectoid, is clearly expressed at greater magnifications (fig.15).

Evaluation of Investigation Results

Structural characteristics and properties of metals of IV-VI periods, especially that of transient metals of the III-VI groups, change lawfully in proportion to the increase in their valence. These metals have body-centered cubical structures due to the presence in/ their/ ions of an outer filled p-subshell, consisting of six electrons oriented orthogonally. In calcium, strontium, lanthanum , titanium,zirconium and hafnium the body centered cubical modification is stable in the range of high tempera tures; in scandium and/ yttrium/ such a structure can be found close to the melting point.

With an increase in the valence of the metal from 1 to 6 as result of separation of all of all valent electrons and increase in excessive nuclear charge the metallic radius decreases continuously (table 5). This is observed in series from potassium to chromium, from/ rubidium/ to molybdenum and from cesium to tungsten. By the same rule decreases also the ion radius,corresponding to higher valence or transition to the anion of all valent electrons. In view of the fact that the

attraction of different in sign charged ions leads to their drawing closer, than the
reaction of cations with electron gas in/ the/ lattice of the metal, effective ion ra-
dii appear to be smaller than the corresponding metal radii.

Thanks to a rise in the number of separating electrons and reduction in ion dimen-
sions, leading to a rise in electron gas density in IV-VI periods in direction from
left to right from I to VI group, is observed a continuous intensification of the
metal bond and a rise in strength/ of/ the body-contered cubical structure (lattice).
This is expressed on one hand in the rise in molting point, boiling point and heat
content at molting point, and, on the other hand, it promotes a rise in such mechanical
strength chara teristics of the lattice, as elasticity modulus, hardness, ultimate
strength etc (see table 5). Such an increase in strength of body contered structure
from alkali metals to metals of the VI group-chromium, molybdenum and tungsten- and
also during the transition to much heavier metals in groups IV-VI is of enormous im-
portance for the development of heat resistant alloys. Heat resistance of metals rises
in direction from the I to the VI group and with the increase in atomic weight within
groups IV-VI, so that the most heat resistant among the transient metals appear to
be niobium, tantalum, molybdenum and tungsten. Hence it is evident, especially, also
the fact, that the reinforcement of niobium and its alloys with 30% Zr by the formation
of solid solutions appears to be more effective, when pentavalent vanadium and hexa-
valent chromium and molybdenum are introduced, as compared with alloying with tetra-
valent titanium.

But the heat resistance and above all the oxidizability of transient metals re-
veal entirely different laws. Let us discuss the thermodynamic properties of higher
oxides of transient metals of III-VII groups (table 6). Judging by their heats of
formation per one bond with O_2 atom, by the molting and boiling points, these oxides
became more stable in direction from right to left (from the VII to the III group)

and from top down.

Fig.14.Microstructure of surface layer,contaminated with oxygon (X 500)
a–niobium; b–Nb+30% Zr; c–Nb+ 30% Zr + 2% Ti; d–Nb + 30+ Zr + 10% Ti.

Fig.15. Perlite like structure of the layer, contaminated with oxygen (X 1000)
a- Nb + 30% Zr + 10% Ti; b- Nb + 30% Zr + 7% Mo; c- Nb + 30% Zr + 10% Mo.

Table 5

Crystalline Structures and Properties of Metals of IV-VI periods [3 - 5]

Period	Characteristic	Group					
		I	II	III	IV	V	VI
	Crystalline structure	K ОЦК 6ТЗК	Ca γ—ОЦК 6ТЗК	Sc β—ОЦК 6ТЗК	Ti β—ОЦК 6ТЗК	V ОЦК 6ТЗК	Cr ОЦК 6ТЗК
	Metallic radius, Å	2.38	1.97	1.60	1.47	1.36	1.28
	Ion radius, Å	1.33*	1.04*	0.83*	0.64*	0.4*	0.35*
	Melting point °C	62.3	850	1538	1667	1730	1890
	Young modulus E, kg/mm²	—	2000	—	11200	14100	21900
	Hardness H, kg/mm²	0.037	30-42		90	80-100	100-130
	Crystalline structure	Rb ОЦК 6ТЗК	Sr γ—ОЦК 6ТЗК	Y β—ОЦК 6ТЗК	Zr β—ОЦК 6ТЗК	Nb ОЦК 6ТЗК	Mo ОЦК 6ТЗК
	Metallic radius, Å	2.51	2.15	1.81	1.6*	1.47	1.40
	Ion radius, Å	1.49*	1.20*	0.97*	0.82*	0.69*	0.62*
	Melting point °C	39	770	1552	1860	2468	2622
	Young modulus E, kg/mm²	240			8700	12000	33250
	Hardness H, kg/mm²	0.022			80	75-100	140-195
	Crystalline structure	Cs ОЦК 6ТЗК	Ba ОЦК 6ТЗК	La γ—ОЦК 6ТЗК	Hf β—ОЦК 6ТЗК	Ta ОЦК 6ТЗК	W ОЦК 6ТЗК
	Metallic radius, Å	2.70	2.24	1.87	1.59	1.47	1.41
	Ion radius, Å	1.65*	1.38*	0.99*	0.82*	(0.68)*	0.65*
	Melting point °C	28.6	710	928	2130	2996	3395
	Young modulus E, kg/mm²	175	1250	3820	7970	19200	35300
	Hardness H, kg/mm²	0.015		37-40		45-125	200-270

Table 6

Thermodynamic properties of higher oxides of transient metals [6,7]

Oxide	Sc_2O_3	TiO_2	V_2O_5	CrO_3	Mn_2O_7
Heat of formation- ΔH_{298}, kcal/mol per at. O_2	138,7±15,0	112,7±1,0	74,1±7,5	46,1±2,5	24,8±2,5
Melting point °C	—	1920	670	195	—
Boiling point, °C	—	2227	Распад. decompos.	—	Распад. decomposition
Entropy S_{298}, kcal/degr mol.	—	12,0±1,0	31,3±0,3	17,2±2,5	—

Oxide....	Y_2O_3	ZrO_2	Nb_2O_5	MoO_3	Tc_2O_7
AS above	151,6±1,5	129,7±1,2	90,7±2,0	59,4±1,5	38,0±4,
	2420	2700	1400	795	120
	4300	4300	—	1100	310
	26,0±2,5	12,1±0,1	32,8±0,2	18,6±0,3	44,0±2,5

Oxide.....	La_2O_3	HfO_2	Ta_2O_5	WO_3	Re_2O_7
As above	143,5±3,0	133±0,5	97,8±2,0	66,7±0,5	42,4±1,0
	2320	2790	1870	1473	296
	4200	—	—	1850	362
	—	14,2±0,1	34,2±0,4	19,9±0,2	49,55±0,1

At other conditions being equal the metal/ ion holds that much less the oxygen atom in the lattice of/ the compound, the greater the number of oxygen atoms per metal atom . An increase in the strength of higher oxides in downward direction with in the groups/ is connected with an increase in the metallic nature of the element at an increase in its atomic number. Table 6 shows, in this way, that the least durable higher oxides are possessed by the most high valence metals of V, VI and VII groups, possessing high/ oxygen valence. In this connection the most high melting and heat resistant transient metals - molybdenum, tungsten and rhenium - form the most

low melting and weak higher oxides; some of these differ in addition by high volatility (MoO_3, WO_3, $Re_2)_7$). This appears to be the main reason for low heat resistance of the most high melting metals, on account of which they require protective coatings. Niobium, like tantalum, has much more durable and high melting higher oxides, and alloying appears to be a sufficiently $\underline{\text{effective}/}$ .means of increasing their heat resistance qualities.

The metal can be heat resistant, if in the subsequent series of its oxides, originating layer by layer on the surface in the process of oxidation, there would be at least one sufficiently strong oxide to form a dense protective layer. The high heat resistance of chromium is due to the formation of a film of the Cr_2O_3 compound, combining $\underline{\text{the high}/}$ heat of formation with sufficient high melting. Still higher$\underline{\text{protective}/}$ properties are possessed by $Cr_2O_3 \cdot FeO$, $Cr_2O_3 \cdot NiO$ types of spinel and others. By studying the thermodynamic qualities of intermediate oxides of niobium ,vanadium and other transient metals it becomes evident that much stronger are ordinarily not higher but lower oxides, namely, monoxides NbO, VO, MnO, sesqui oxides Cr_2O_3 and others (table 7). Monoxides of transient metals possess, as a rule, a simple structure of the NaCl type, clearly expressed metallic properties, promoting a $\underline{\text{strong}/}$ bond with the lattice of $\underline{\text{the}/}$ very metal, and the ability to reinforce by being alloyed with other metals. Evidently, the effective method of increasing the effectiveness of the protective NbO layer can be the alloying of niobium with such elements (metals),which have the same outer electronic ion configuration, as does niobium, they possess the body centered cubical structure and contribute by their valent electrons. In view of the fact, that the ratio $r^0 : r_{Nb} = 2,0$ is unfavorable for the formation of an NaCl type structure NbO has up to 25% of oxygen vacancies, and the introduction of metals with smaller ion radii, than in niobium, will promote a rise in density and in the protectiveness of the monooxide layer. From this view point titanium, vanadium, chro-

nium and molybdenum, selected in/ <u>role of/</u> additions to the niobium alloy with 30% Zr

appeared to be most perspective. A further way of increasing the heat resistance may

lie in direction of formation of durable spinels between NbO, VO and Cr_2O_3, Al_2O_3 mo-

nooxides.

Of the chosen alloying elements vanadium and molybdenum form with niobium conti-

nuous series of solid solutions from room temperature to melting point, with a mini-

mum on the liquidus and solidus curves. Zirconium and titanium in the range of high

temperatures (above 1000° and 600° respectively) also form with niobium continuous

series of solid solutions, since their high temperature beta-modifications are iso-

morphic relative to the structure of niobium, and the ratio of atomic radii also

appears to be favorable.

At temperatures below indicated in alloys of the Nb-Zr, Nb-Ti system there are

polymorphis conversions, due to the appearance of conr + hexagonal alpha-phase.

Zirconium stabilizes the high temperature beta-phase and the moderately hardened (in

air) niobium alloy with 30% Zr has the structure of beta-solid solution. Chromium,

as well as niobium, possesses body centered cubical structure, but the difference in

atomic radii, exceeding 15%, leads to the limitation of solid solution zones and to

the appearance of a $NbCr_2$ compound.

Additions of 2-10% vanadium, molybdenum, titanium or chromium to the niobium al-

loy with 30% Zr, apparently, promote a rise in stability of the solid solution with

body centered cubical structure. Consolidation of the transient metal base solid solu-

tion, e.g. niobium base, as result of the effect of alloying with other transient me

tals,, e.g. zirconium, titanium, vanadium, chromium and molybdenum, is due to a series

<u>of/</u> causes, and above all to the valence of the alloying transient metal, to the dimension

of its atom, structure of outer electron shells, concentration of electron gas etc.

The values of atomic radii of the used transient metals are such: Nb -1,47;

Table 7

Thermodynamic Characteristics of Oxides of Transient Metals [54]

Group 1

Oxide	Heat of format kcal/mol = 1 bond	Entropy S298 cal/deg mol	Oxide melt.pt °C
Ti	-	7,3	-
TiO	123,9	8,3	1667
Ti₂O₃	129,36	-	2020
Ti₃O₅	-	-	
TiO₂	112,7	12,0	1920
Zr	-	9,3	1860
ZrO	-	-	
ZrO₂	129,7	12,1	2700
Hf	-	13,1	2130
HfO₂	133	14,2	2790

Group 2

Oxide	Heat of format	Entropy	Oxide melt.pt °C
V	-	-	-
VO	108	7,0	1730
V₂O₃	98,7	9,3	1700
V₂O₄	93,75	-	1970
V₂O₅	74,1	31,3	670
Nb	-	-	-
NbO	97,5	8,73	2468
NbO₂	94,7	11,5	1945
Nb₂O₅	90,7	13,0	1915
		32,8	1490
Ta	-	9,9	2996
Ta₂O	-		
Ta₂O₅	97,8	34,2	1870

Group 3

Oxide	Heat of format	Entropy	Oxide melt.pt °C
Cr	-	-	-
Cr₂O₃	90	5,68	1800
CrO₂	69,6	19,4	(2300)
CrO₃	46,1	-	185
		17,2	
Mo	-	-	-
MoO₂	60,0	6,83	2622
Mo₂O₃	-		
MoO₃	52,1	18,6	795
W	-	-	-
WO₂	65,0	8,0	3395
W₂O₅	64,8	16,0	~1600
WO₃	66,7	19,9	1473

Group 4

Oxide	Heat of format	Entropy	melt.pt °C
Mn	-		
MnO	92	7,6	1245
Mn₂O₃	-	14,3	1785
MnO₂	-		gas >535
Mn₃O₄	24,8		
Tc	-	7,5	
TcO₂	51,7	15,0	
TcO₃	43,0	17,0	-
Tc₂O₇	35,0	44,0	120
Re	-	8,9	
ReO₂	50,7	17,4	3170
ReO₃	27,7	-	160
Re₂O₇	42,4	49,5	296

Zr - 1,60; Ti - 1,47; Mo - 1,40; V - 1,36; Cr - 1,28 Å.

~~Strengthening/~~
of niobium with elements, forming with it solid solutions, as shown
~~direct/~~
by theory, is in / dependence upon the atomic radius of the alloying element and
the amount of admixture.

Alloying of niobium with zirconium strengthens same as result of considerable dif-
~~solution/~~
ference in atomic radii. Subsequent alloying of the solid/ of the alloy (Nb +
30% Zr) with elements, forming with niobium solid solutions, shows, that additions
of Cr, V and Mo do best strengthen the binary alloy. The obtained results can be ex-
plained by the strengthening of the crystalline niobium lattice and of the niobium-
zirconium alloy as result of the difference in atomic radii of niobium and alloying
admixture. Chromium, the atomic radius of which is much smaller, than in niobium,
causes also a considerable rise in tenacity as result of maximum distortion of the
crystalline lattice.

Atomic radii of titanium and niobium are approximately identical, consequently
titanium alloying of the binary alloy leads only to a slight rise in hardness. An
increase in the amount of Cr, Mo or V in solid solution leads to a rise in hardness
(see fig.1).

An increase in hor hardness of the Nb + 30%Zr alloy at 500 and 1000° in compari-
son with the niobium, apparently, can also be explained by the presence of the degree
of distortion of the niobium lattice as result of the difference of atomic radii, and
also by the presence of valance of the alloying element (see table 3).

By comparing the graphs of gains in the process of oxidation at 500° it becomes
evident, that all ternary alloys have shown approximately identical gaisn after 20
hours of exposure. It is therefore difficult to separate out the best alloy. But it
can be mentioned that at 2% additions to is binary alloy maximum increase in oxida-
tion resistance is offered by vanadium. At 5 and 10% alloying admixture the best re-

STOP HERE   STOP HERE

sult is shown by Cr. The difference in gains in all alloys constitutes 1-2 c/m^2, consequently it can be said, that under given conditions the stability of all investigated alloys is approximately of the same order of magnitude. The best alloy in these conditions appears to be the one which offers a dark protective film.

When testing the oxidizability of alloys at 1000° took place a sharp division of alloys with respect to stability. Gain analysis shows, that / the best / effect on an increase of scaling resistance of the binary alloy, within the limits of the investigated / concentrations. / are admixtures of 10% Ti, 7% Mo and 5% V. The strongest effect on the increase in scaling resistance of the binary alloy is produced by an admixture of 7% Mo. / which / reduced in half the gain in comparison with 10% Ti and 5% V admixtures; furthermore, it promotes the formation of a dense gray / non-peeling / oxide layer.

A rise in oxidizability of ternary alloys with an increase in vanadium and molybdenum admixture to above optimum takes place as result of formation of / volatile / V_2O_5 and MoO_3 oxides. Of all the investigated alloys / the best / one was found to be a quaternary niobium alloy with 10% Zr, 10% Ti and 10% Mo, which showed minimum gain and excellent surface state after 20 hoursof testing at 1000°. During oxidation on this alloy is formed a thin dense gray non-peeling oxide layer. The remaining alloys showed less satisfactory / results. /

A comparison of rates of oxidation of the investigated ternary / alloys / with the / rates / of oxidation of binary alloys (by literature sources) is given in table 8. As is evident, 30% additions of Zr to binary niobium/titanium, niobium/molybdenum and niobium/chromium alloys lead to a considerable improvement in scaling resistance of the alloys; an exception here are niobium/vanadium alloys, 30% Zr additions to which do not improve the scaling resistance.

The nature of the rate of oxidation curves of the investigated ternary alloys coincides qualitatively with the corresponding rate of oxidation curves for binary

alloys. However, in ternary alloys the minimum rate on alloys with vanadium shifted from 10 to 5%, and in alloys with Mo - from 5 to 7%.

Table 8. Comparing rates of oxidation at 1000° of ternary alloys (in accordance with data of this report) and binary alloys (by literature data) [1]

Composition of alloy, %	Rate of oxidation $g/m^2 \cdot hr$	Time of exposure hr
Niobium [1,2]	242	
Niobium	229,9	20
Nb + 35 Zr	300	5
Nb + 30 Zr	245,5	5
Nb + 5 Tl	157,0	5
Nb + 30 Zr + 5 Tl	92,6	5
Nb + 10 Tl	77	10
Nb + 30 Zr + 10 Tl	42,2	10
Nb + 5 V	46	10
Nb + 30 Zr + 5 V	55,2	10
Nb + 10 V	35,0	10
Nb + 30 Zr + 10 V	299,5	10
Nb + 5 Cr	281	5
Nb + 30 Zr + 5 Cr	176,6	5
Nb + 10 Cr	262	5
Nb + 30 Zr + 10 Cr	106,2	5
Nb + 5 Mo	46	20
Nb + 30 Zr + 5 Mo	36,3	20
Nb + 10 Mo	101	5
Nb + 30 Zr + 10 Mo	78,4	5

Alloying/ of binary alloys with 30% Zr reduced the depth of oxygen contamination, in alloys with titanium by 1-0.2 mm, and in binary alloys with chromium, vanadium and molybdenum by approximately two times. In published data the niobium alloy with 35% Zr showed a depth of contamination of the order of 0.05 mm, while investigations have revealed, that the depth of oxygen contamination on the niobium + 30% Zr alloy equals 0.33 mm.

In the investigated alloys the depth of contamination lies between 0.3 - 0.4 mm. A sharp reduction in the depth of contamination on the Nb + 30% Zr and 10% V alloy is due to greater rate of oxidation, at which the process of metal conversion into oxide is much faster than the process of contamination. An increase in the alloying

admixture slows down the process of metal conversion into oxide, as result of forma-
tion of more protective oxide films, which consequently may cause a rise in layer
contamination depth. On the investigated alloys after/ the removal/ of the oxides is
revealed a dark sub layer, which does not separate from the sample, the structure
of which has not finally explained. According with the announcement of one of the
authors, this is a mixture of NbO and Nb_2O_5 oxides, others assume the presence of an
oriented Nb_2O_5 with a deviation from the stoichiometric composition. When pickling
the microscopic sections the sublayer remaining on the samples has well conducted
current, which indicates its sufficient metallic nature.

On alloys, having shown excellent oxidation resistance, after removal of the
closely/
/adhering thin gray oxide film was also detected a dark sublayer. As the exposure time
increases the rate of alloy oxidation decreases, although on the alloys is formed
a cracking peeling off oxide film, which cannot serve as adequate protection. This
offers basis to assume, that the process of oxidizing niobium alloys, apparently, is
controlled by the properties of the sublayer. A certain effect on the reduction of
the rate of alloy oxidation, most likely, can be produced also by the/ calcining of the
oxides , which took place on many alloys.

Oxidation of the metal, apparently, takes place on the sublayer-oxide boundary,
because the mark left on the sample, was well preserved on the oxide film and was
not covered by reaction products, thus indicating the diffusion of oxygen into the
depth of the metal. On the sublayer-oxide boundary takes place the formation of Nb_2O_5
type oxide of this or any other modification, as result of oxygen diffusion through
the oxide film and diffusion of niobium ions through the sublayer. On alloys, having
shown good results and being coated during oxidation by a gray dense thin non-peel
ing oxide film, the slowing down of the rate of oxidation is, apparently, / influenced
also by the growth in oxidelayer thickness. The oxidation process in this case is

controlled by the sublayer and by the growing ability of the surface layer as well.

Destruction of oxide layers on samples of /investigated/ alloys takes place basical
ly as result of origination in the film of internal stresses, as result of greater
volumetric Nb_2O_5 coefficient. On the cylindrical surface of the sample as result of
oxide film growth originate tensile stresses, leading to radial cracks. On the faces
of the sample the oxide layer is by one side firmly connected with the metal, hinder
ing its growth, which may cause compression stresses in plane, parallel to the face.
As the oxide layer grows the increasing magnitude of these stresses leads to shearing
of the oxide layers along these surfaces. Alloying may impart to the oxide layer a
greater mechanical strength, plasticity, and also change the volumetric coefficient
of the forming oxide. Formation of such oxide films results in a considerable rise
in scaling resistance of the alloy.

Oxygen contamination of niobium and alloys on niobium basis takes place, most
likely, as /result/ of oxygen diffusion from the /oxide film/ into the metal. The oxygen
contaminated metal layer, represents a solid solution of oxygen in niobium. The addi-
tion of 30% Zr impart to the contaminated metal layer a lamellar type structure, which
is, possibly, /connected/ with the separation of dissolved oxygen in form of zirconium
and niobium oxides. Alloying of niobium with 30% Zr sharply reduces the rate of metal
/conversion/ into oxide, and also considerably reduces /the rate/ of oxygen diffusion in
metal, as result of which in the contaminated layer is produced such a concentration
of oxygen, which exceeds its solubility limit in the given alloy, which, naturally,
leads to separation of niobium oxides and oxides of the alloying element in form of
flakes, resembling an eutectoid. Alloys without zirconium or with a lesser content
of same have after oxidation a sharply outlined contaminated layer, the structure
of which is not /lamellar/ but represents a solid solution with separations.

To increase the scaling resistance of niobium the alloying should be done by

such admixtures, which would assure in the initial moment of oxidation the creation of a protective heat resistant oxide layer with possibly smaller number of vacancies. It was found that protective oxide layers are produced by admixtures of elements with smaller ion radii than in niobium (0.69 Å), namely, vanadium (0.4 Å), molybdenum (0.62 Å)and chromium (0.35 Å). Here is necessary to take into consideration the solubility of the alloying element in the oxide of the basic metal and the thermodynamic stability of the oxide of the alloying element.

If it is assumed, that the rate of niobium oxidation is limited by the diffusion of oxygen through the NbO monooxide film, then the main problem appears to be a reduction in defectiveness of this oxide, in which about 25% of the units are not occupied by much larger oxygen ions and appear to be vacancies, facilitating oxygen diffusion to the metal. Such a porosity of NbO lattice is due, apparently, to the unusually large ratio of anion and cation radii r_o/r_{Nb} = 2, which lies beyond the limit, favoring the formation of NaCl type structures.

The NbO monooxide has the NaCl type structure with parameter a = 4,203 Å, corresponding to the doubled sum of ion radii (0,69 + 1,32 = 2,01Å), by its structure it appears to be stable only after removal of a part of oxygen atoms,which reduces stress and lattice distortion. Substitution in such a lattice a part of niobium ions by ions of metals with smaller ion dimension, but with very same and improved outer p-similarities, offers the possibility of filling up the vacancies with oxygen ions.

Consequently additions of titanium, vanadium (in small amounts),chromium and molybdenum promote the obtainment of a more dense and more protective monooxide film with lower number of vacancies; such additions do effectively raise the scaling resistance of niobium and its alloys with zirconium. A certain favorable effect of zirconium, having a greater ion radius, than niobium, is due, apparently, to the high strength of its dioxide, which appears on the surface of the alloy at sufficient

ly high zirconium concentration. For the /very/ same reasons a comparatively high vanadium and molybdenum content decreases the scaling resistance of niobium as result of appearance of unstable natural V_2O_5 and MoO_3 oxides. In complex alloys the effect of various factors is much more difficult to be taken into consideration.

Conclusions

1. Investigated was the /effect/ of additions of alloying elements - titanium, /vanadium,/ chromium and molybdenum- in quantities of from 2 - 10 at.% on the scaling resistance and oxygen contamination of binary alloy ofniobium with 30 at.% of Zr.

The investigation was conducted at temperatures of 500 and 1000° with heating in the air and /exposures/ of 1, 3, 5, 10 and 20 hours.

2. Oxidation of niobium at 500° follows thelinear law and is characterized by very high rates of oxidation, or the order of 22 g/m^2.hr. Alloying of niobium with 30% Zr raises its scaling resistance at 500° by more than 40 times. Additional alloying of the Nb+ 30%ZR with admixtures of 2-10% titanium, vanadium, chromium or molybdenum increases the scaling resistance of the alloy at 500° by 1.5 times as compared with the binary alloy.

3. Unalloyed niobium at 1000° has an extremely high rate of oxidation,equalling 230 g/m^2.hr. Introduction of 30 at.% of Zr reduces 20-hr gain from 4600 to 3150 g/m^2 i.e. a total of 1.5 times. Additional alloying of the Nb+30% Zr alloy with admixtures of 2-10% Ti and Cr considerable raises its scaling resistance. Additions of molybdenum and /vanadium/ to 7 and 5 at % respectively increase the scaling resistance of the Nb+30% Zr, but at a fyrther increase in their concentration the scaling resistance /decreases./

4. Alloying of niobium with 30% Zr decreases the depth of oxygen penetration for 20 hrs at 1000° from 4.5 mm to 0.33 mm. Additional alloying ofthe binary alloy with admixtures of titanium, vanadium, chromium and molybdenum only slightly changes the

depths of oxygen penetration.

5. In the process of /oxidation/ at 500° on niobium is formed a porous white scale. Addition of 30% Zr leads to the formation during oxidation of a dark protective oxide layer. Additional alloying /of the/ binary alloy with titanium, vanadium, chromium and molybdenum brings practically no changes to the outer appearance of the oxide film.

6. At 1000° and 20-hr exposure a niobium sample with a diameter of 15 mm and 5 mm in height oxidizes entirely. On remaining alloys is formed a thick cracking scale. With the increase in content of the third alloying element in the niobium + 30% Zr alloy, the thickness of the oxide film decreases.

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